Effect of Fire Retardants on Heat Release Rate of Wood Flour-Polyethylene Composites

Nicole M. Stark, Scott A. Mueller, Robert H. White, and Tim A. Osswald

Abstract

Wood-plastic composites (WPCs) represent a growing class of materials used by the residential construction industry and the furniture industry. For some applications in these industries, the fire performance of the material must be known, and in some cases improved. There is considerable information available on the fire performance for wood and plastics separately. However, the fire performance of wood-plastic composites is not well understood, and there is little information available in the literature. Determining the heat release rate (HRR) is one way to characterize the fire performance of wood-plastic composites. In this study, we determined the HRR for wood flour-polyethylene composites, and compared the results with unfilled polyethylene and solid wood. We then evaluated the effect of several additive-type fire retardants on the HRR.

Introduction

Wood-plastic composites (WPCs) represent an emerging class of materials that combines the favorable performance and cost attributes of both wood and plastics. These products are resistant to moisture, insects, decay, and warping when compared with traditional pressure-treated lumbers. Wood-plastic composites are stiffer, exhibit less creep, and are more dimensionally stable than unfilled plastic lumber (Clemons 2002). In addition, WPCs offer a "wood" look and feel with minimum maintenance when used as exterior decking. Due to these attributes, forest-products companies see WPCs as a way to increase the value-added utilization of waste wood and wood of low commercial value. Plastic processors see wood as a readily available, relatively inexpensive filler that can lower resin costs, improve stiffness, increase profile extrusion rates, and act as an environmentally friendly way to decrease the use of petroleum-based plastics (Clemons 2002).

Currently, several commercial WPCs are manufactured for the residential construction industry, primarily as lumber for decking, siding, roof tiles, and window profiles. Manufacturers are also introducing new applications for the furniture industry. To expand into the residential construction industry and develop applications for the furniture industry it is critical to understand the fire performance of WPCs, and in some cases to improve it.

The fire performance of plastics has been well characterized. While burning, plastics can melt and drip, providing other ignition sources. One strategy to improve the fire performance of plastics is to use additive-type fire retardants. Additive-type flame retardants are added to the plastic melt during processing and come in many forms, although most flames retardants for plastics are particles or powders. Additive-type flame retardants can improve fire performance through the following mechanisms: 1) redirect decomposition and combustion reactions toward the evolution of non-combustible gases, or heavy gases that interfere with the interchange of combustion gases and air, 2) redirect the decomposition and combustion reactions

Stark:
 Research Chemical Engineer, USDA Forest Service, Forest Products Laboratory, Madison, Wisconsin, USA
Mueller:
 Engineering Technician, USDA Forest Service, Forest Products Laboratory, Madison, Wisconsin, USA
White:
 Research Forest Products Technologist, USDA Forest Service, Forest Products Laboratory, Madison, Wisconsin, USA
Osswald:
 Kuo K. and Cindy F. Wang Professor, University of Wisconsin–Madison, Dep. of Mechanical Engineering, Madison, Wisconsin, USA

toward reducing the heat of combustion, 3) maintain the physical integrity of the material, and 4) increase the specific heat or thermal conductivity (Hilado 1998).

The compounds which have been found to be most effective in producing flame retardance are compounds containing bromine, chlorine, or phosphorous, or combinations of two or more of these elements. Other elements which have exhibited some flame-retardant effect are antimony, boron, nitrogen, silicon, and zinc. These elements are often used with phosphorous or halogenated compounds.

Halogenated compounds based on chlorine and bromine are effective flame retardants. While there are environmental concerns regarding the use of these materials, bromine-based fire retardants are still widely used in polyolefins. Bromine-based retardants act in the gaseous phase to redirect or terminate chemical reactions involved in combustion. Heavy-bromine gases also protect the material from exposure to oxygen and heat (Hilado 1998). Bromine-based flame retardants are practically always used with an antimony synergist, often antimony trioxide. Antimony compounds alone do very little but in combination with halogens they form antimony trihalides in the vapor phase. Antimony trihalides react with atomic hydrogen to hinder oxygen.

Metal hydroxides are another common flame retardant. Metal hydroxides are typically aluminum- or magnesium-based. Aluminum interferes with oxidation reactions while magnesium is most effective as a smoke retardant. Both aluminum and magnesium are more effective as hydrated compounds. Decomposition of both aluminum hydroxide and magnesium hydroxide produces water and water vapor. The water vapor dilutes gaseous fuel products. The heat required for dehydration also contributes to the fire retardant capabilities (Hilado 1998). High loading levels of metal hydroxides increase the overall heat capacity of the material. Metal hydroxides perform as smoke reducers through the adsorption of carbon materials.

Boron-based flame retardants are generally char producers. The presence of boron can redirect decomposition to increase the production of carbon rather than carbon monoxide or carbon dioxide. By creating a surface layer of char, boron helps block oxygen from the surface and slows the escape of gases (Hilado 1998). Boron can additionally work along with zinc in zinc borate compounds to reduce smoke production. Unlike metal hydroxides, zinc borate compounds often contain water of hydration, i.e., water that can be removed by heating without changing the chemical makeup of the compound. The heat required for dehydration also contributes to the fire retardant capability.

Phosphorous compounds generally increase the amount of carbonaceous residue or char formed. The result is either redirection of decomposition reactions in favor of reactions yielding carbon over carbon monoxide or carbon dioxide and formation of a protective surface layer of char which inhibits access to oxygen. It has been found that phosphorous does not increase char in polyolefins, unless there is another char-forming additive present. Phosphorous is often used with nitrogen-containing compounds, as the combination has proven synergistic. Melamine is sometimes compounded with phosphates to achieve a phosphorous-nitrogen synergism. Melamine assists flame retardance in several ways while decomposing. It creates endothermic reactions and scavenges free radicals. Decomposition produces nitrogen and ammonia, which dilutes fuel gases. Melamine aids in char formation. Ammonium polyphosphate (AP) is another compound that takes advantage of the phosphorous-nitrogen synergism. Ammonium polyphosphate is known to cause an intumescent response and is commonly used in coatings. In a heated environment, an intumescent material will foam, creating a barrier which blocks heat and oxygen from the flammable surface, improving the function of charring. Ammonium polyphosphate lowers smoke production and helps resist flame migration. Along with the majority of nitrogen-containing compounds, AP is known to give off ammonia during burning.

The limited number of studies available on fire performance of WPCs indicates a need for a comprehensive investigation into the matter. Studies conducted on commercial samples show that WPC lumber performs better than unfilled plastic lumber in fire tests (Malvar et al. 2001; Fabian 2008), but worse than solid wood (White et al. 2007). Typically, the composition of the commercial lumber is proprietary. The type of plastic matrix used and wood content may be known, but the additive type and content is not. Because some WPCs are used in building applications where fire performance standards must be met, it can be assumed that flame retardants have been used in some commercially available WPCs.

The number of studies conducted on manufactured WPCs (where the fire-retardant type and concentration is known) is limited, but these studies show that fire retardants can be effective at improving fire performance. The halogenated compound based on bromine, used in combination with antimony oxide, has proven effective at improving the oxygen index of WPCs (Shen and Olson 2006). The reported effectiveness of metal hydroxides in WPCs has been mixed. Sain et al. (2004) reported an improvement in oxygen index with the incorporation of magnesium hydroxide while Abu Bakar et al. (2006) reported no positive effect on fire retardancy with the addition of magnesium hydroxide. Aluminum hydroxide has been shown to decrease WPC burning speed (Garcia et al. 2009). Boron-based compounds in the form of zinc borate have been studied primarily in combination with other fire retardants. Sain et al. (2004) found that a partial replacement of magnesium hydroxide with zinc borate decreased the oxygen index, lowering fire performance. Shen and Olson (2006) found that a partial

substitution of a bromine-based fire retardant with zinc borate resulted in an increase in fire performance, while partial substitution of a phosphorous-based compound with zinc borate decreased the WPC fire performance. Most research investigating fire retardants for WPCs has focused on phosphorous-based compounds. Comparisons between AP and melamine phosphate showed that AP was most effective at increasing the oxygen index of WPCs (Li and He 2004). Others have also reported positive effects of fire retardancy with use of AP (Abu Bakar et al. 2006, Shen and Olson 2006).

The studies that evaluated fire retardants for WPCs have shown that fire performance can be improved. However, it is impossible to compare the various classes of fire retardants because the studies evaluated WPCs with different matrix materials and fire-retardant contents using a range of fire performance tests. The main goal of this research project was to create a baseline of information about the fire performance of WPCs and the effectiveness of fire retardants. Specific objectives included characterizing the heat release rate (HRR) of wood-polyethylene composites and evaluating various classes of fire retardants for use in wood-polyethylene composites.

Experimental Methods
Materials and Manufacturing Method

The base WPCs consisted of polyethylene (PE), wood flour (WF), and a lubricant. The PE had a 5 melt flow index and was purchased from ExxonMobil (HD 6605.70, Houston, TX). American Wood Fibers supplied the 40 mesh, mixed pine wood flour (AWF 4020, Schofield, WI). Struktol Company of America supplied the lubricant (TPW 113, Stow, OH). In addition, five fire retardant systems were investigated:

1) Decabromodiphenyl oxide (Saytex 102E, Albemarle Corp., Baton Rouge, LA) and antimony trioxide (BrightSun HB, China Antimony Chemicals Co., Ltd., Guangxi, China)

2) Magnesium hydroxide (Magnifin H-10, Albemarle Corporation, Baton Rouge, LA)

3) Zinc borate (FireBrake ZB, Rio Tinto Minerals, Valencia, CA)

4) Melamine phosphate (Melapur MP, Ciba Specialty Chemicals, Tarrytown, NY)

5) AP (Exolit AP 422, Clariant Corporation, Charlotte, NC)

The formulations examined are shown in **Table 1**. To maintain good surface characteristics of the composites, a lubricant was added to each formulation. Composites without fire retardants had either 50 or 60% by weight WF. Composites with fire retardants incorporated 50% WF and 10% of the fire-retardant system. This allowed composites to be compared on the basis of WF content

Table 1. ~ *Formulations of WPCs manufactured with fire retardants.*

| | Composition based on weight (%) | | | | | | | | |
Code	PE[†]	WF	BR	AT	MH	ZB	MP	AP	Lub
PE	100								
WF-50	45	50							5
WF-60	35	60							5
WF-BR	35	50	7.5	2.5					5
WF-MH	35	50			10				5
WF-ZB	35	50				10			5
WF-MP	35	50					10		5
WF-AP	35	50						10	5

[†]PE = Polyethylene; WF = wood flour; BR = decabromodiphenyl oxide; AT = antimony trioxide; MH = magnesium hydroxide; ZB = zinc borate; MP = melamine phosphate; AP = ammonium polyphosphate; Lub = lubricant.

(50%) or PE content (35%). Unfilled PE samples were manufactured to provide a control.

A 32-mm Davis Standard (Pawcatuck, CT) twin-screw co-rotating extruder combined with a Schenck AccuRate (Whitewater, WI) loss-in-weight feeder system was used for all compounding. The barrel of the extruder had 10 separate zones, with zones 4 and 9 vented to the atmosphere. The screw had a 36:1 L/D ratio consisting primarily of conveying elements, with kneading and mixing elements incorporated into the screw before the vents to build up pressure and disperse and mix the components. The extruder was outfitted with a strand die; the strand extrudate was cooled in a water slide and pelletized. The composites were compounded in two steps. In the first step, PE was compounded with or without fire retardant. This was to ensure thorough mixing of the fire retardant in the polymer. The melt temperature ranged from 192 to 201°C while the melt pressure ranged from 3.6 to 4.5 MPa. Before the second compounding step, the WF was dried for 24 h at 105°C. The dried WF was then compounded with lubricant and PE with or without fire retardant as shown in **Table 1**. During the second compounding step the melt pressure ranged from 188 to 199°C while the melt pressure ranged from 4.2 to 7.0 MPa. Adding magnesium hydroxide or zinc borate resulted in higher melt pressures while adding melamine phosphate resulted in lower melt pressures.

To form composite boards, the compounded pellets were dried before being processed into boards using a Davis Standard 89-mm single-screw extruder. The melt temperature ranged between 167 and 174°C. The extrudate was formed using a 12.7 mm × 127 mm (1/2" x 5") radius-edge profile die.

Fire Performance Tests

Cone calorimetry was performed on an Atlas Cone 2 Combustion Analysis System (Atlas Electrical Devices, Chicago, IL) according to ASTM E1354 (ASTM 2008). WPC samples were cut from the extruded boards to a

size of 100 mm × 100 mm. The sample thickness was as extruded, at 12.7 mm. Samples were exposed in the horizontal orientation with the conical radiant electric heater located 25 mm above the specimen and the retainer frame (without the wire grid) over the test specimen. The sides and bottom of the samples were wrapped in aluminum foil. Each sample rested on an insulatory fiber blanket to keep it apart from the holder during the test. A spark igniter started the burning process and the length of time required to create a steady flame was recorded. Three replicate samples were tested at a heat flux level of 50 kW/m^2. The exhaust system flow rate was 0.024 m^3/s. For PE samples, data collection for the first replicate ended when it was visually observed that there was very little material in the foil wrapper. Due to a high HRR, data collection for the remaining two replicates was stopped early, but not before 300 s after specimen ignition. For the WPCs, data collection for all samples was stopped once the mass loss rate dropped below 1.5 g/m^2 s^{-1}. The WPC ceased burning once the heat from the cone was removed. For reference, pine boards cut to 100 × 100 × 12.7 mm were also subjected to fire performance testing.

The primary result from the cone calorimeter test is a HRR vs. time curve. Heat release rate is defined as the heat evolved from the specimen per unit time, and is determined by the oxygen consumption during burning (ASTM 2008). For reporting purposes, the heat release curve was reduced to single numbers via the initial peak HRR and averages of the HRR over a set time (60 s, 300 s, and over the test duration) after ignition of the specimen was observed. Ignitability was determined by observing the time for sustained ignition of the specimen, and is reported as ignition time (IT).

Results and Discussion

Representative HRR curves for PE and WPCs (WF-50 and WF-60) are shown in **Fig. 1**. For comparison, a representative HRR curve for solid pine is included. Examination of the HRR vs. time shows that the HRR of PE started increasing later than the HRR of WPCs or pine. However, the HRR of PE increased much more quickly than that of WPCs or pine. The HRR of PE continued to increase until the material was consumed, while the HRR of WPCs reached a peak early during the test duration, then burned more slowly during the test duration. The peak HRR of PE was much higher than the peak HRR for solid pine. The peak HRR for WPCs fell between that of PE and solid pine.

The HRR results for PE, WPCs (WF-50 and WF-60), and solid pine is shown in **Table 2**. The peak HRR of PE was much higher than that of WPCs and solid wood. A comparison between the two WPCs showed that the WPC with more wood (60 versus 50%) had a lower peak HRR. This is consistent with an earlier study that reported a decrease in HRR with increasing wood content (Stark et

al. 1997). It is interesting that 60 s after ignition, the average HRR was higher for the WPCs than for the solid pine or PE. However, 300 s after ignition and for the duration of the test, the average HRR of WPCs was lower than the average HRR of PE and higher than the average HRR of pine. This was because the WPCs reached their peak HRR during the first 60 s after ignition, while the HRR of PE increased throughout the test duration. The IT for WPCs and solid pine was similar, and lower than the IT for PE. The results suggest that although it takes longer for the PE to ignite compared with the WPCs, once ignition is underway the PE burns faster than the WPCs.

Representative HRR curves for the WPCs with and without fire retardants are shown in **Fig. 2**. It is easily seen that all fire retardants lower the HRR of WPCs. Overall, the AP improved the HRR the most, but also led to a much longer test duration. An expansion of the HRR peak (**Fig. 3**) shows a broad range of peak HRRs. WPCs containing the bromine-based fire retardant had the highest peak HRR while WPCs containing magnesium hydroxide had the lowest.
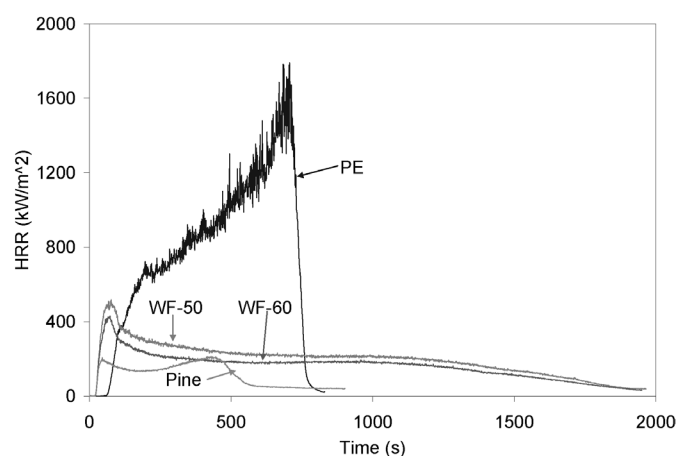

Figure 1. ~ *Representative HRR curves for unfilled polyethylene, 50 and 60% wood flour-polyethylene composites, and solid pine.*

Table 2. ~ *Heat release rate (HRR) results for unfilled polyethylene, 50 and 60% wood flour-polyethylene composites, and solid pine.*

		Average HRR			
	Peak HRR	60 s	300 s	Total test	IT
		kW/m^2			s
PE	1790[†]	284 (21)	635 (32)	893[†]	82.2 (9.5)
WF-50	505 (18)[‡]	369 (13)	326 (7)	202 (7)	24.5 (0.3)
WF-60	437 (15)	315 (3)	260 (1)	167 (7)	24.9 (0.3)
Pine	209 (2)[¶]	171 (11)	157 (8)	139 (7)	22.2 (2.1)

[†]Data for one sample only.

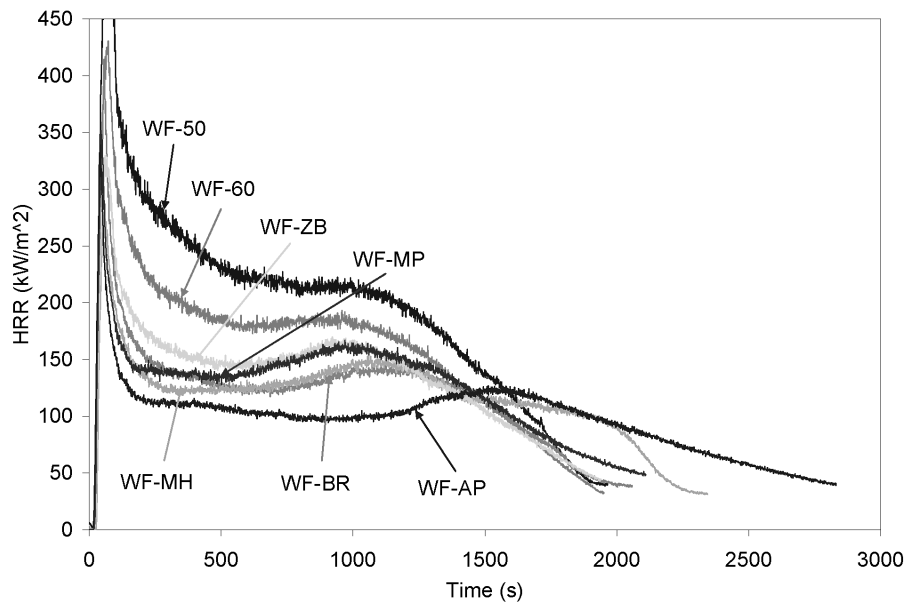[‡]Numbers in parentheses represent one standard deviation.

[¶]First peak.

Figure 2. ~ *Representative HRR curves for 50 and 60% wood flour-polyethylene composites and for 50% wood flour-polyethylene composites with 10% fire retardant.*
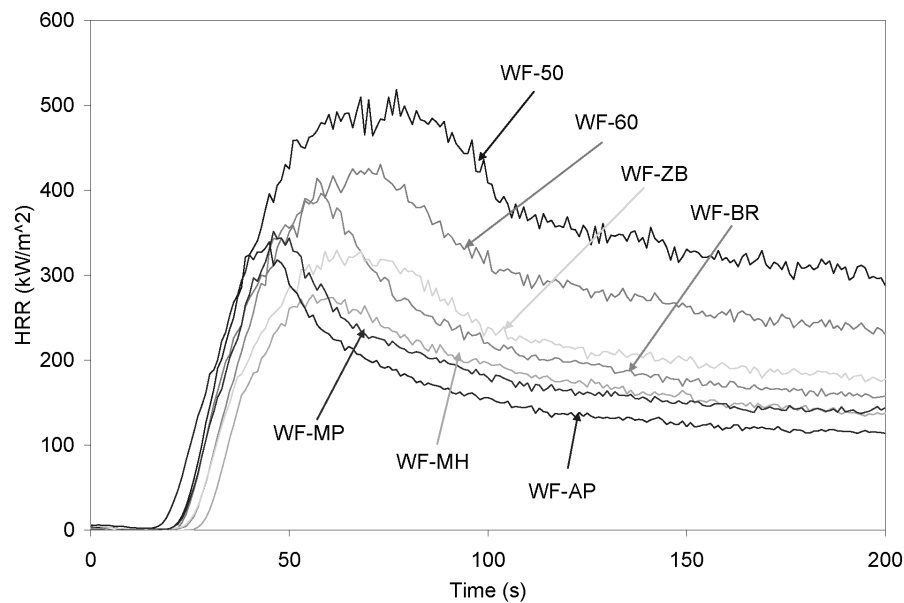

Figure 3. ~ *Expansion of the peak of representative HRR curves for 50 and 60% wood flour-polyethylene composites and for 50% wood flour-polyethylene composites with 10% fire retardant.*

Figure 4 summarizes the peak HRR as well as the HRR averaged over 60 s, 300 s, and the test duration once ignition was observed. Each bar represents the average of three replicates and the error bars represent one standard deviation. All fire retardants significantly improved the peak HRR and average HRRs of WPCs. Because the PE content has a large effect on HRR, it is useful to compare results between WPCs with the same PE content. In our case, WF-60 and WPCs containing fire retardants all had a 35% PE content. Compared with WF-60, the peak HRR of WPCs decreased between 11 and 35% when fire retardants were added. WPCs containing magnesium hydroxide performed the best while WPCs containing the brominated compound performed the worst. Fire retardants also influenced the average HRR over the total test duration. Compared with WF-60, the average HRR

decreased between 19 and 39% when fire retardants were added. For average HRR, AP improved the fire performance of WPCs the most while zinc borate improved the fire performance the least.

The ignition time of WPCs is summarized in **Fig. 5**. The average of three replicates is shown with the error bars representing one standard deviation. The ignition time of WF-50 and WF-60 were similar. Adding fire retardants to WPCs had a mixed effect on IT. Fire retardants that improved the IT (i.e., increased it) include the brominated compound, zinc borate, and magnesium hydroxide. Melamine phosphate and AP decreased the IT. Compared with WF-60, the best and worst performers were magnesium hydroxide (increasing the IT by 24%) and AP (decreasing the IT by 12%).

Figure 4. ~ *Calculated Heat Release Rate (HRR) data for 50 and 60% wood flour-polyethylene composites and for 50% wood flour-polyethylene composites with 10% fire retardant.*
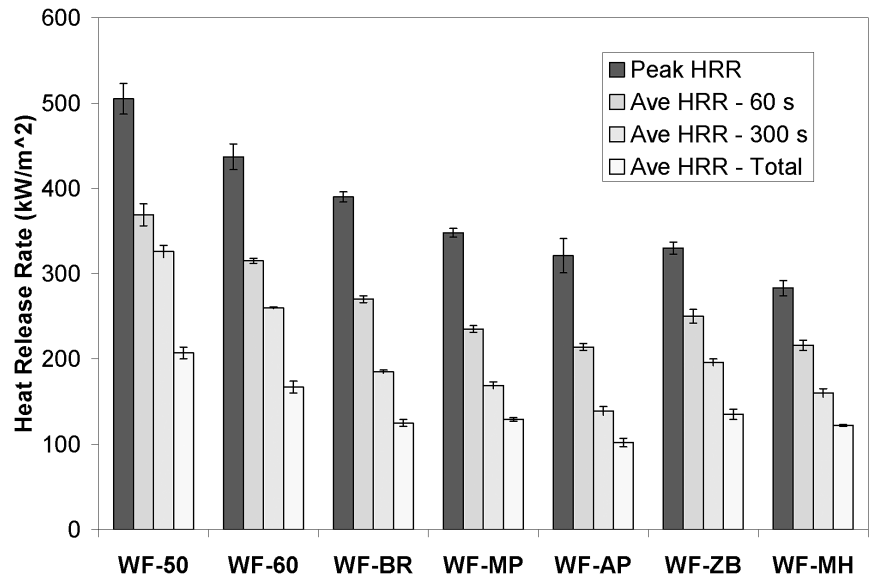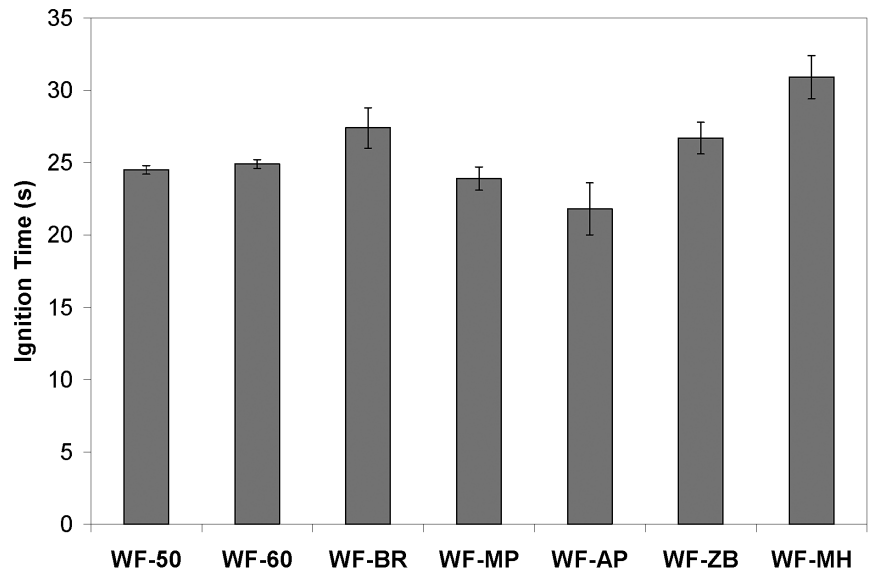

Figure 5. ~ *Ignition time for 50 and 60% wood flour-polyethylene composites and for 50% wood flour-polyethylene composites with 10% fire retardant.*

Summary

There is potential for WPCs to expand into new and existing applications in the residential construction and furniture industries. However, little knowledge regarding the fire performance of WPCs limits this expansion. In this study, we used cone calorimetry to determine the HRR for WF-polyethylene composites. We also evaluated the effect of five additive-type fire retardants systems on the HRR.

Wood-polyethylene composites generally exhibit lower HRRs than unfilled PE but higher HRRs than wood. However, the peak and average HRR for the test duration of WPCs was closer to wood than PE. Compared with unfilled PE, the ignition time of WPCs was shorter and 60 s after ignition the average HRR was higher. As the tests continued, the HRR of unfilled PE increased rapidly until the material was consumed, while the HRR of WPCs reached an initial peak and then decreased slowly. The peak HRR of PE was decreased by 72% when 50% wood was added and 76% when 60% wood was added.

All fire retardant systems examined improved the HRR of WPCs. Some fire retardant systems improved the IT while others did not. The following summarizes the performance of fire retardants in WPCs on the basis of PE content. Compared with 60% WF-polyethylene composites, fire retardants in WPCs behaved in the following ways:

- Magnesium hydroxide improved the peak HRR the most, while the brominated compound improved peak HRR the least.
- For the test duration, AP improved the average HRR the most while zinc borate improved the average HRR the least.

- Magnesium hydroxide increased the ignition time the most while AP decreased the ignition time the most.

This study provides a baseline of HRR performance of WPCs. It also demonstrates the types of changes that can be obtained when various fire retardants are incorporated into WPCs. While fire performance can be improved by adding fire retardants, the addition of WF into PE can dramatically improve the fire performance of PE. For example, incorporating 60% wood into PE lowered the peak HRR of PE by 76%. In comparison, incorporating 50% wood and 10% magnesium hydroxide (the fire retardant that had the most effect on peak HRR) decreased the peak HRR of PE by 84%.

Acknowledgments

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